

Full Paper

Volatile Surfactant-Assisted MOCVD: Application to LaAlO_3 Thin-Film Growth**

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A new approach to the CVD of oxides with kinetically hindered diffusion, called volatile surfactant-assisted (VSA) metal-organic chemical vapor deposition (MOCVD), consisting of film deposition in the presence of a volatile low melting point oxide (Bi_2O_3) has been developed. The process was applied to the deposition of LaAlO_3 films, and a model of the process was proposed. Epitaxial and textured LaAlO_3 films on various substrates were obtained, both by thermal and VSA MOCVD. A marked improvement in crystalline quality and surface morphology was found for the films deposited by VSA MOCVD. LaAlO_3 films obtained in the presence of Bi_2O_3 did not contain Bi. A significant increase (up to five times) of the deposition rate was observed for LaAlO_3 films deposited by VSA MOCVD compared with that for the films grown by thermal MOCVD.

Keywords: MOCVD, Lanthanum aluminate, Diffusion enhancement, Volatile surfactant, Oxide thin films

1. Introduction

The growth of thin films from a gas phase by various deposition techniques results in different film morphologies, textures, and crystallinity. Crystal growth theories regard these properties as being dependent on the interplay of condensation rate and diffusion mobility in the growing film. When diffusivity in the growing film is not high enough to accommodate the flow of the substance coming to the substrate from the gas phase, a polycrystalline or amorphous film grows instead of an oriented or epitaxial one (provided that crystallographic requirements to epitaxy are met). The homologous temperature, which is the ratio of deposition temperature T_d to melting temperature T_m , can be used as a measure of diffusivity in the growing film. The Tamman rule says that diffusion-activated processes in solids become active at temperatures of about $0.8\text{--}0.6 T_m$. At typical deposition temperatures not exceeding 1000°C , it is always difficult to obtain films of high crystalline quality for the phases with high melting temperatures. To solve this problem, diffusion mobility in the growing films must be enhanced.

In some physical vapor deposition (PVD) techniques such as pulsed laser deposition, or ion beam or magnetron

sputtering, surface mobility in the growing films is increased due to bombardment of the film surface by energetic particles. Several approaches of non-thermal activation, which affect surface mobility and/or process chemistry, have been developed for CVD, namely, plasma-,^[1] photo-,^[2] ultraviolet-,^[3] and laser-activation,^[4] etc. In our recent study,^[5] we proposed heterovalent doping, creating a high concentration of ion vacancies in the structure of the material being deposited, as a way to enhance diffusion mobility in the growing film. Both PVD and CVD activated processes allow crystalline films to be obtained at relatively low temperatures.

Lanthanum aluminate ($T_m = 2100^\circ\text{C}$) is an example of a phase with almost no diffusion at conventional deposition temperatures, but it could have a prospective application as a buffer layer for the growth of various perovskite films such as high-temperature superconductors, ferroelectrics, metal-conducting oxides, and colossal magnetoresistance oxides.^[6] However, there have been few reports of the successful deposition of LaAlO_3 films of high crystalline quality. The only reports in the literature to date have been of epitaxial LaAlO_3 films grown by pulsed laser deposition (PLD),^[6,7] radio frequency (RF) magnetron sputtering,^[8] and sol-gel^[9] on perovskite substrates (SrTiO_3 and LaAlO_3 itself). Attempts to grow LaAlO_3 on Si, MgO , Al_2O_3 , CeO_2 , and YSZ led to amorphous, or at best polycrystalline, films.^[6,7] Recently, Malandrino et al. succeeded in obtaining highly (111) oriented LaAlO_3 films on (001)YSZ substrates by thermal MOCVD at 1050°C ,^[10] as well as (001) LaAlO_3 films on (001) SrTiO_3 .^[11]

We tried to accelerate the diffusion mobility in the MOCVD of LaAlO_3 films by changing the film growth mechanism to one close to vapor-liquid-solid. It was accomplished by film deposition in the presence of volatile low melting point oxide; in our case bismuth oxide Bi_2O_3 was selected. This approach to diffusion and crystallization

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Chemical Vapor Deposition

enhancement was used for the first time in our previous study on the MOCVD of BaTiO_3 films.^[12] At the first stage of this work, the experiments on thermally activated MOCVD in the absence of Bi_2O_3 were performed in the temperature range 800–1050 °C.

2. Results and Discussion

2.1. LaAlO_3 Films Deposited Without BiPh_3 : X-ray Diffraction Characterization

LaAlO_3 films were deposited on a number of substrates with different structure types: perovskite type (001) NdGaO_3 , (110) SrTiO_3 ; fluorite type (001)YSZ and fluorite type buffer layers (001) PrO_x /(001)YSZ and (001) CeO_2 /(1 $\bar{1}$ 02) Al_2O_3 ; NaCl type (001) MgO ; and on R-sapphire (1 $\bar{1}$ 02) Al_2O_3 . Deposition parameters used are listed in Table 1.

Table 1. Parameters of the deposition process.

Parameter	Value
Deposition temperature [°C]	800–1050
Total pressure [mbar]	20
Total gas flow [L h^{-1}]	20
Partial pressure of O_2 [mbar]	10
Deposition time [min]	20–30
Solvent consumption [mL h^{-1}]	20
Total precursor concentration [mol L^{-1}]	0.02
Evaporation temperature [°C]	250

All films with composition close to the stoichiometry obtained at 950 °C and higher, on all the substrates used, were crystalline. Thus, we succeeded in depositing crystalline LaAlO_3 films not only on perovskite type substrates but also on the substrates of other structural types, the films deposited at 1000 °C being epitaxial or highly oriented, as will be shown below. The crystalline quality of the films decreased dramatically with even slight deviations of the film composition from molar ratio $\text{Al/La} = 1:1$. Off-stoichiometric films were amorphous. At the lower deposition temperature 900 °C, only LaAlO_3 films on perovskite type substrates NdGaO_3 were found to be crystalline. As-deposited amorphous films crystallized over a 2 h annealing period at 1000 °C, which again indicated low diffusion mobility of lanthanum aluminate under the deposition conditions.

We believe that correct composition of the films and high growth temperature allowed us to deposit, for the first time, oriented LaAlO_3 films on a number of substrates by thermal MOCVD.

2.1.1. Perovskite-Type Substrates: NdGaO_3 and SrTiO_3

Neodymium gallate has a good crystallographic match with LaAlO_3 (mismatch 2.45 %). At 1000 °C we obtained high-quality epitaxial (001) LaAlO_3 /(001) NdGaO_3 films as indicated by XRD θ -2 θ and ϕ scans (Fig. 1A,B), and the

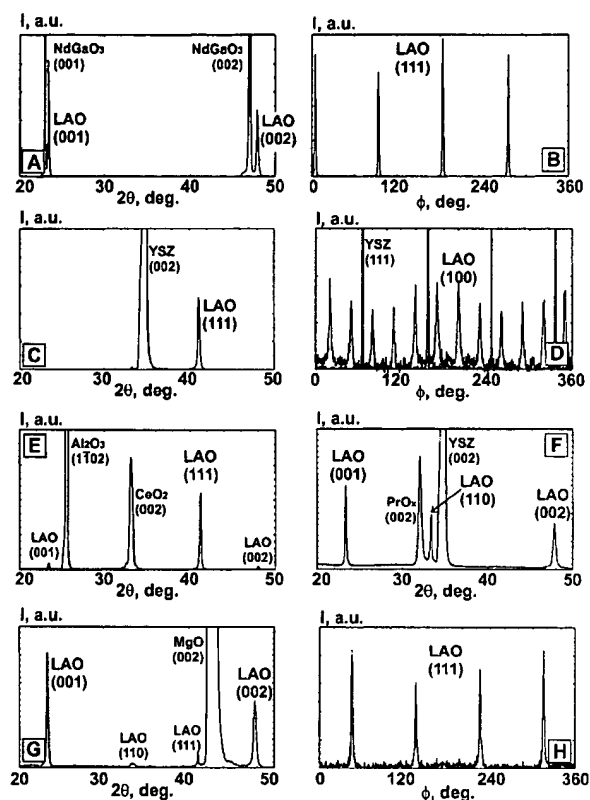


Fig. 1. XRD data for LaAlO_3 films deposited at 1000 °C: A) θ -2 θ scan for (001) LaAlO_3 /(001) NdGaO_3 . B) ϕ scan for (001) LaAlO_3 /(001) NdGaO_3 confirming in-plane alignment. C) θ -2 θ scan for (111) LaAlO_3 /(001)YSZ. D) ϕ scan for (111) LaAlO_3 /(001)YSZ, revealing two type in-plane alignment. E) θ -2 θ scan for (111) + (001) LaAlO_3 /(001) CeO_2 /(1 $\bar{1}$ 02) Al_2O_3 . F) θ -2 θ scan for (001) + (110) LaAlO_3 /(001) PrO_x /(001)YSZ. G) θ -2 θ scan for (001) LaAlO_3 /(001) MgO . H) ϕ scan for (001) LaAlO_3 /(001) MgO , confirming in-plane alignment.

LaAlO_3 (002) rocking curve full width at half maximum (FWHM) value of 0.54°. At 900 °C, crystalline LaAlO_3 films were obtained on NdGaO_3 ; moreover, despite low XRD peak intensity, the films were highly (001) textured. LaAlO_3 films grown at 900 °C on the other substrates were amorphous.

We also deposited LaAlO_3 films on another coherent perovskite substrate (110) SrTiO_3 at 1000 °C. According to the XRD data, (110) LaAlO_3 /(110) SrTiO_3 films were obtained.

It is not surprising that the best results in the growth of perovskite LaAlO_3 films can be obtained on coherent perovskite substrates, because there is only a slight difference in lattice constants, which does not favor epitaxy, whereas, in the case of other substrates, the difference in the structure of the matching lattices is also very important.

2.1.2. Fluorite-Type Substrate: YSZ and Buffer Layers PrO_x and CeO_2

Films obtained on (001)YSZ at 950 °C were polycrystalline, at 1000 °C (111)-oriented LaAlO_3 films were grown. As is seen from the XRD ϕ scan (Fig. 1D), there are two

equivalent in-plane orientations for (111)LaAlO₃ growth on (001)YSZ. The following epitaxial relations were established: (111)LaAlO₃//(001)YSZ, $\langle\bar{1}10\rangle$ LaAlO₃// $\langle 100\rangle$ YSZ; and (111)LaAlO₃//(001)YSZ, $\langle\bar{1}10\rangle$ LaAlO₃// $\langle 010\rangle$ YSZ.

Matching of oxygen positions in the (001)substrate plane and the (111)LaAlO₃ plane is shown schematically in Figure 2. Six {100}-type planes of pseudo-cubic lattice give rise

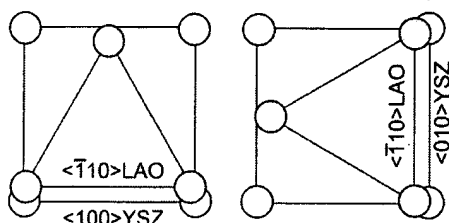


Fig. 2. Model of oxygen cell lattice matching for (111)LaAlO₃ and (001)YSZ planes. Epitaxial relations are as follows: (111)LaAlO₃//(001)YSZ, $\langle\bar{1}10\rangle$ LaAlO₃// $\langle 100\rangle$ YSZ; (111)LaAlO₃//(001)YSZ, $\langle\bar{1}10\rangle$ LaAlO₃// $\langle 010\rangle$ YSZ.

to six symmetrical peaks in the ϕ scan with maxima at $n \times 60^\circ$. Due to the presence of two epitaxial in-plane variants, which can be made coincident by 90° rotation around the [001]YSZ direction, twelve peaks are present in the resulting ϕ scan (with maxima at $n \times 60^\circ$ and $n \times 60 + 90^\circ$). The same growth behavior had previously been reported for another perovskite-on-fluorite heteroepitaxial pair (111)BaTiO₃/(001)YSZ.^[12] It is interesting to note that perovskites with lattice parameter values between those for LaAlO₃ ($a = 3.79$ Å) and BaTiO₃ ($a = 3.94$ Å, $c = 4.04$ Å) such as CaRuO₃ and (La_{1-x}Pr_x)_{0.3}Ca_{0.7}MnO₃,^[13] exhibit different preferential axial alignment (110)perovskite/(001)YSZ.

Two types of texture were found in LaAlO₃ films grown on fluorite-type buffer layer CeO₂/(1102)Al₂O₃, only (00 ℓ) and ($h h h$) reflections were present on θ -2 θ scans (Fig. 1E), the latter texture being stronger. Interestingly, (00 ℓ) and (110) two type textured LaAlO₃ films were obtained on another fluorite-type buffer layer PrO_x/(001)YSZ (Fig. 1F). A similar result had previously been reported for BaTiO₃ films: (111)BaTiO₃/(001)YSZ, (111) + (00 ℓ)BaTiO₃/(001)CeO₂/(1102)Al₂O₃, and (00 ℓ)BaTiO₃/(001)PrO_x/(001)YSZ oriented films had grown.^[12]

2.1.3. NaCl Structure Type Substrate: MgO

We succeeded in depositing (001)LaAlO₃/(001)MgO films at temperatures not lower than 1000 °C, as illustrated by XRD θ -2 θ and ϕ scans (Fig. 1G,H). It should be noted that (001)-oriented LaAlO₃ films are very promising as buffer layers for the deposition of various perovskite films on MgO substrates. Such a buffer layer may change the preferred orientation of perovskite growth on MgO from polycrystalline or slightly textured to epitaxial.

2.1.4. Corundum Structure Type Substrate: α -Al₂O₃

In the deposition temperature range 950–1000 °C, we obtained polycrystalline LaAlO₃ films without any pronounced texture, which we assume is due to the large structural mismatch between these materials.

2.2. LaAlO₃ Films Deposited Using VSA MOCVD

2.2.1. MOCVD of LaAlO₃ Films in the Presence of BiPh₃: Comparison with Bi-free Depositions

We estimated the partial pressure of Bi₂O₃ in the reactor, assuming that the whole amount of BiPh₃ precursor reacted in the vicinity of the substrate to produce Bi₂O₃. By this estimation we got the highest possible value of Bi₂O₃ partial pressure. BiPh₃ transport to the reactor was achieved with no condensation of bismuth oxide on the substrate, i.e., the Bi₂O₃ partial pressure was lower than the Bi₂O₃ equilibrium pressure under the deposition conditions. In fact, the gaseous phase over condensed Bi₂O₃ contains a number of species: Bi₂O₃, Bi, BiO, Bi₄O₆, etc.^[14] We used data from Kazenas and Chizhikov^[14] for the total equilibrium Bi₂O₃ pressure, P_{sat} , and estimated the relative partial pressure, $P_r = P(\text{Bi}_2\text{O}_3)/P_{\text{sat}}$, for each deposition run.

As expected, energy dispersive X-ray (EDX) and Rutherford back-scattering (RBS) analyses detected no Bi in LaAlO₃ films deposited in the presence of BiPh₃ (Fig. 3). This correlated with the prediction of thermodynamics because the Bi₂O₃ partial pressure in the reactor was kept below the Bi₂O₃ equilibrium pressure. The next important result we got was a significant increase of the film deposition rate in the presence of BiPh₃, compared with that for the films deposited without BiPh₃ with the same supersaturation in the reactor. A deposition rate increase of up to five times (from 0.5 $\mu\text{m h}^{-1}$ for depositions without BiPh₃ to 2–2.5 $\mu\text{m h}^{-1}$ for depositions in the presence of BiPh₃) was observed. This approach has great potential in that it achieves high deposition rates with minimal consumption of precursors.

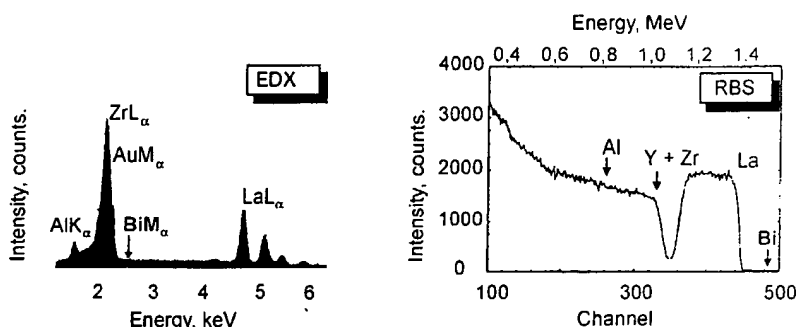


Fig. 3. EDX and RBS spectra demonstrate the absence of bismuth in the LaAlO₃/(001)YSZ films deposited in the presence of BiPh₃.

More importantly, crystalline quality and surface morphology were found to improve remarkably for LaAlO_3 films deposited in the presence of BiPh_3 . Thus, LaAlO_3 films obtained at relatively low temperatures (800–900 °C) without BiPh_3 were amorphous, whereas deposition in the presence of BiPh_3 resulted in crystalline films. According to XRD θ - 2θ and ϕ scans, epitaxial LaAlO_3 films at 950–1000 °C were obtained both with and without the addition of BiPh_3 to the starting solution. The addition of BiPh_3 led to a pronounced increase in the epitaxial quality of the films as indicated by FWHM values of XRD rocking curves, high-resolution electron microscopy (HREM), and atomic force microscopy (AFM) data. Comparison of the results for the LaAlO_3 films, deposited at various BiPh_3 feeding rates, demonstrates progressive decrease of FWHM values of (002) rocking curves with the increase of P_r value: 0.65°, 0.52°, and 0.42° at $P_r = 0, 0.1$, and 0.2, respectively (Fig. 4). HREM investigation showed higher mosaicism and less perfect interface structure in $\text{LaAlO}_3/\text{NdGaO}_3$ films grown without BiPh_3 (Fig. 5). AFM also revealed a remarkable difference in surface morphology, indicating higher surface diffusion of the film components during growth in the presence of Bi-containing vapor. The films deposited in the presence of BiPh_3 had smoother surfaces (they were characterized by lower values of root-mean-square roughness, see Fig. 6).

It is worth reiterating that all these results were obtained for films deposited in the presence of BiPh_3 at a growth rate four to five times higher than that for those deposited without BiPh_3 . This fact emphasizes how strongly the diffusion mobility in the growing film can be accelerated by the approach proposed.

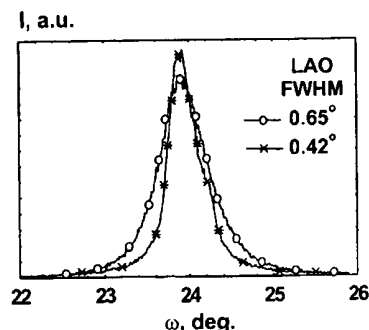


Fig. 4. XRD rocking curves for (002) reflections of (001) LaAlO_3 /(001) NdGaO_3 epitaxial films deposited at 950 °C with (—x—) and without (—○—) the addition of BiPh_3 . The FWHM value of the rocking curve of the film deposited in the presence of Bi_2O_3 is notably smaller.

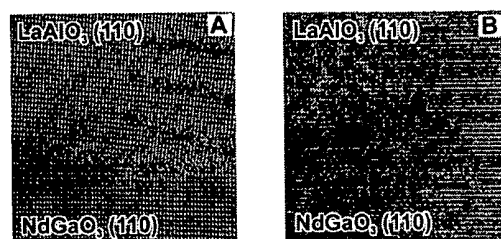


Fig. 5. HREM images of the interfaces of (001) LaAlO_3 /(001) NdGaO_3 epitaxial films deposited at 950 °C: A) without Bi_2O_3 and B) in the presence of Bi_2O_3 .

2.2.2. Proposed Mechanism of Diffusion Mobility Enhancement: VSA MOCVD

The mechanism of diffusion mobility enhancement in MOCVD (in the presence of Bi_2O_3 formed from BiPh_3)

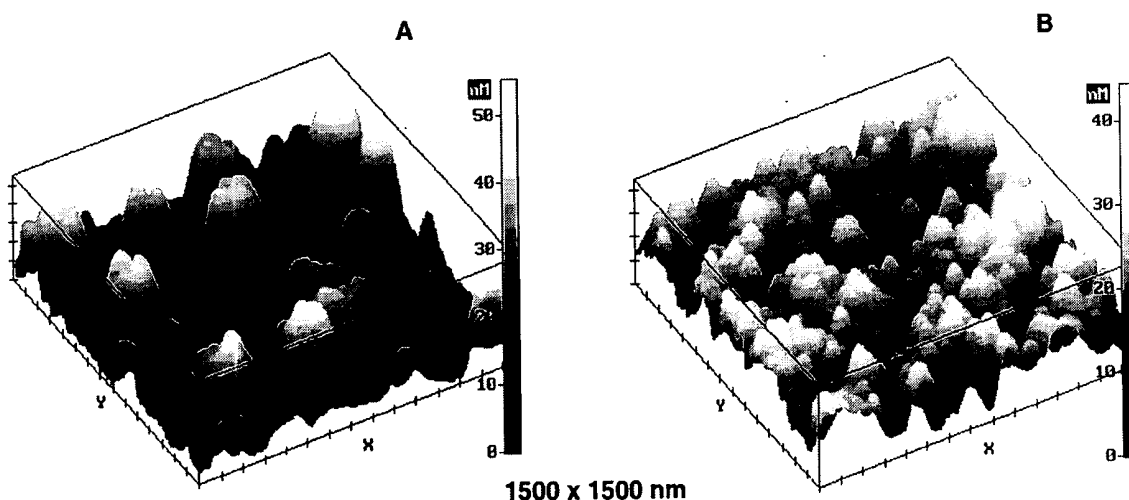


Fig. 6. AFM data on the surface morphology of (001) LaAlO_3 /(001) NdGaO_3 epitaxial films deposited at 950 °C: A) without Bi_2O_3 , root-mean-square roughness $S_a = 8.8$ nm, and B) in the presence of Bi_2O_3 ($P_r = 0.2$), $S_a = 5.9$ nm.

should be clarified. The proposed model of this process is shown schematically in Figure 7.

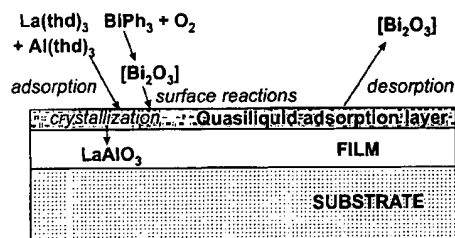


Fig. 7. Proposed mechanism of VSA MOCVD. The model involves adsorption of the precursors, surface reaction producing oxides, formation of a quasiliquid adsorption layer with Bi_2O_3 , which enhances the crystallization, and desorption of volatile Bi_2O_3 .

We assume that BiPh_3 molecules from the bulk gas flow diffuse through the boundary layer and adsorb on the substrate surface; hence surface reaction takes place, producing bismuth oxide. Other MOCVD reaction products are being formed from the other precursors at the same time (in our case LaAlO_3) but, importantly, these condensed particles are not yet crystalline. Bismuth oxide has a low melting temperature (820°C) and is known to form low melting point eutectics with many oxides. Liquid Bi_2O_3 is widely used as a solvent for many oxides in crystal growth by the flux technique.^[14] At the deposition temperatures employed in this study, there should be a certain amount of liquid phase on the substrate: LaAlO_3 solution in Bi_2O_3 . Then, crystallization of LaAlO_3 occurs from the melt. The mobility of the film components is, naturally, much higher in the liquid phase than on the solid substrate surface. There are numerous examples of crystal growth acceleration owing to the presence of a liquid, the vapor–liquid–solid (VLS) technique^[15] being one of the most prominent ones. Consequently, we expected the crystal quality of the resulting film to be essentially higher in the case of crystallization assisted by liquid, and this was clearly confirmed by our experimental results. Moreover, the sticking coefficient for adsorption of the precursors on the substrate covered with liquid should be much higher than that for adsorption on the solid substrate surface at the same precursor concentration in the gas phase. This is the most probable explanation of the observed increase of the deposition rate in the presence of BiPh_3 , as in the case of VLS (whisker growth).

Bi_2O_3 has a sufficiently high saturation vapor pressure to evaporate continuously from the substrate. Because the Bi_2O_3 partial pressure in the reactor was kept lower than the Bi_2O_3 equilibrium pressure by feeding in appropriate amounts of BiPh_3 precursor, no condensation of bulk liquid Bi_2O_3 occurs during the deposition. There is a dynamic steady state on the substrate: liquid Bi_2O_3 forms and evaporates continuously. Very similar behavior has been described in the literature: under appropriate conditions, self-limiting incorporation of Bi during deposition of Bi-containing ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$,^[16] and superconductor

$\text{Bi}_2\text{Sr}_2\text{CuO}_y$,^[17] films occurred. That is, no extra stoichiometric Bi deposited (despite a large extra flux of Bi) because the partial pressure of corresponding Bi-containing particles in vapor was kept higher than their equilibrium pressure over the film compounds, and lower than that over pure Bi or Bi_2O_3 .

Thus, we believe it is more correct to speak about a more or less thick quasiliquid Bi_2O_3 surface adsorption layer, than about a bulk amount of liquid. This adsorption layer can “dissolve” LaAlO_3 to some extent, making its diffusion mobility much higher, which improves the crystal quality of the film. Additionally, continuous evaporation of Bi_2O_3 from the substrate provides supersaturation of the adsorption layer with the dissolved film components necessary for their crystallization.

The approach that we propose seems to resemble surfactant mediated layer-by-layer growth in the molecular beam epitaxy (MBE) of semiconductors and metals.^[18,19] The term “surfactant” is used here in a rather broad sense to denote a surface impurity substance that is added in amounts not exceeding one monolayer, and promotes layer-by-layer growth under conditions at which island homo- or heteroepitaxial growth usually occurs. A good surfactant must float on the surface of the growing film without being incorporated, and must not form a separate phase. These conditions are met when the effective bond strengths satisfy the inequalities $V_{A-A} > V_{A-S} \gg V_{S-S}$, where A and S are adatoms of the growing substance and the surfactant atoms, respectively.^[20] Although the mechanisms of surfactant-mediated epitaxy and the approach to MOCVD proposed by us can be essentially different, we believe the criteria of applicability for volatile low melting point oxides should be almost the same as those for surfactants; therefore, we decided to use the term “surfactant” (in an analogous, broad sense) to denote volatile low melting point oxides in our approach.

We proposed the term volatile surfactant-assisted MOCVD (VSA MOCVD) for this version. The crystal growth mechanism in VSA MOCVD has obviously many common features with VLS and flux techniques. Consequently, the main approaches and considerations developed for these techniques^[15,16] may be useful also in VSA MOCVD. On the other hand, there are some clear distinctions. First, in VSA MOCVD, there is no bulk liquid phase, which makes it possible for Bi_2O_3 to cover the entire substrate surface uniformly without combining in separate droplets, as in VLS. Second, liquid surfactant Bi_2O_3 is produced on the substrate in situ, not the case in the aforementioned techniques. It enhances the crystallization, making the film components more mobile, and leaves the substrate completely by the end of the process.

There is a limitation to the proposed approach that should be mentioned here: the volatile surfactant chosen should not form stable compounds, or an extended solid solution range, with the components of the film to be obtained (this is expressed by $V_{A-A} > V_{A-S}$). In this work,

from a number of volatile low melting point oxides, we chose bismuth oxide; however, there are possible surfactants that might prove interesting, such as PbO, MoO₃, Ti₂O₃, etc. It is also interesting to try combinations of oxides (e.g., PbO + Bi₂O₃), like the complex solvents in the flux technique.

3. Conclusions

We have developed volatile surfactant-assisted MOCVD, a new approach to the CVD of oxide films with kinetically hindered diffusion, first proposed in our previous work.^[12] The approach involves film deposition in the presence of a volatile low melting point oxide, in our case Bi₂O₃ was selected. The process was applied to the deposition of LaAlO₃ films, and a model of the process was proposed.

We succeeded in the deposition of epitaxial and textured LaAlO₃ films on various substrate materials, both by thermal and VSA versions of MOCVD. The following axial orientations were found in the films: (001)LaAlO₃/(001)NdGaO₃; (001)LaAlO₃/(001)MgO; polycrystalline LaAlO₃/(1102)Al₂O₃; (111)LaAlO₃/(001)YSZ; (111) + (001)LaAlO₃/(001)CeO₂/(1102)Al₂O₃; (001) + (110)LaAlO₃/(001)PrO₃/(001)YSZ.

The crystalline quality and surface morphology were found to improve remarkably for the films deposited in the presence of Bi₂O₃, compared with those grown without Bi₂O₃. According to EDX and RBS analysis, LaAlO₃ films obtained in the presence of Bi₂O₃ did not contain Bi. Significant increase (up to five times) of the film deposition rate was observed for LaAlO₃ films deposited in the presence of Bi₂O₃, compared with that for the films grown without Bi₂O₃.

The experimental results obtained thus far are in good agreement with the proposed VSA MOCVD mechanism although they cannot be considered to be final confirmation since further study of the mechanism, using direct observation, is necessary. On the other hand, we believe that VSA MOCVD shows potential as a method of obtaining various oxide films. Judging by the results obtained, VSA MOCVD is a promising method of depositing high-quality epitaxial films, crystalline films of the phases with kinetically hindered diffusion, and growing films and coatings at high deposition rates.

4. Experimental

Film depositions were carried out with a single aerosol source MOCVD setup, described in detail elsewhere [21], which has been used to deposit various oxide films such as YBa₂Cu₃O_{7-x}, Bi₂Sr₂CaCu₂O_x [21], (La_{1-x}Pr_x)_{0.7}

Ca_{0.3}MnO₃ [13], La_{1-x}Sr_xCoO₃ [22], and BaTiO₃ [12]. Briefly, a solution of the precursors is nebulized ultrasonically and the aerosol thus produced flows with the Ar carrier gas into a heated tube where evaporation of the solvent and precursors takes place. The vapor is transported through heated lines by Ar flow into the vertical cold wall reactor. A solution of La(thd)₃, Al(thd)₃, and, in some experiments, BiPh₃ precursors in diglyme was used. In order to avoid ligand exchange with BiPh₃, 3 vol.-% Hthd was added in the starting solution [12].

The films were characterized by XRD θ -2 θ and ϕ scans, and rocking curve and pole figure measurements performed with a Siemens D5000 four circle diffractometer with a secondary graphite monochromator (Cu K α radiation). Film microstructure and composition were studied using a CAMSCAN scanning electron microscope equipped with an EDAX system for quantitative analysis. RBS spectroscopy (Van der Graaf accelerator, 1.5 MeV He⁺ ions) was used to analyze traces of the surfactant in the films, film thickness, and composition. Transmission electron microscopy was performed with a Philips CM30ST electron microscope operating at 300 kV and equipped with a field emission gun and side-entry $\pm 25^\circ$ tilt specimen holder. The film thickness was also measured using an alpha-step 200 profilometer (Tencor Instruments) and estimated from EDX spectra. The surface morphology was studied using AFM (P4-SPM-MDT, Nanotechnology MDT Inc., Russia).

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